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Downhole Heavy Crude Oil Upgrading Using CAPRI: Effect of Steam upon Upgrading and Coke Formation

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ABSTRACT: Heavy crude oil and bitumen are characterized by a low yield of light distillates in the range of 10–30% with a boiling point below 350 °C, high density (low API gravity), high viscosity, and high heteroatom content, which impede their exploitation. In this study, the catalytic upgrading process in situ (developed by the Petroleum Recovery Institute, Canada) add-on to the toe-to-heel air injection for the extraction and upgrading of heavy oil and bitumen downhole was investigated. The effect of steam addition and steam-to-oil ratio upon upgrading, coke formation, sulfur and metal removal were examined using a Co–Mo/ γ -Al₂O₃ catalyst at a reaction temperature of 425 °C, pressure of 20 bar, gas-to-oil ratio of 500 mL·mL⁻¹, and steam-to-oil ratio in the range of 0.02–0.1 mL·mL⁻¹. It was observed that the coke content of the spent catalyst reduced from 17.02 to 11.3 wt % as the steam-to-oil ratio increased from 0.02 to 0.1 mL·mL⁻¹ compared to 27.53 wt % obtained with only nitrogen atmosphere after 15 h time-on-stream. Over the same range of conditions, 88–92% viscosity reduction was obtained as steam-to-oil ratio increased compared to 85.5% in nitrogen atmosphere only, a substantial reduction from the value of 1.091 Pa·s for the feed oil. It was also found that although desulfurization increased from 3.4% in a steam-free atmosphere to 16–25.6% over the increasing range of steam flows investigated, demetallization increased from 16.8% in a steam-free environment to 43–70.5% depending on the increasing steam-to-oil ratio.

1. INTRODUCTION

World oil demand is expected to increase by more than 40% by 2025.¹ As the world's conventional light crude oil production approaches its peak, exploitation of vast deposits of heavy oil and bitumen remains one of the mitigating options to offset the rise in demand.² However, heavy oil and bitumen cannot be refined by present refineries without upgrading processes that first convert them to synthetic light crude oil in order to meet refinery feedstock specification.³ This is because heavy oil and bitumen are characterized by high density/low API gravity, high viscosity, high asphaltene and heteroatom content. Additionally, their production has been retarded because: (1) production costs for heavy oil and bitumen are much higher than conventional light oil; (2) a significant amount of energy is needed to extract and transport heavy oil and bitumen; (3) the environmental challenges such as greenhouse gases associated with heavy oil and bitumen exploitation need to be addressed.²

In this regard, the major cost associated with heavy oil and bitumen exploitation is the additional cost incurred for the surface upgrading facility.⁴ Thermal enhanced oil recovery (EOR) processes are the most widely used for heavy oil and bitumen recovery, which include: steam flooding, steam assisted gravity drainage (SAGD), cyclic steam stimulation (CSS), and in situ combustion (ISC). These processes all rely on viscosity reduction through heating to improve oil flow and production. The produced oil from the aforementioned technologies requires the addition of expensive diluents to aid pipeline transportation to refineries as well as further upgrading to meet refinery feedstock specification. Additionally, 2–5 barrels of water are injected as steam to produce every barrel of oil in SAGD, which makes it very energy-intensive with a large environmental burden.⁵

In situ upgrading of heavy oil and bitumen in the reservoir could present a number of advantages, such as use of available heat and gases, reducing the requirement for surface upgrading and production of low-viscosity oil that can be transported without diluent addition. The toe-to-heel air injection (THAI) process and its catalytic version catalytic upgrading process in situ (CAPRI) are thermal EOR techniques developed over the last 10–15 years which combine thermal recovery and in situ catalytic upgrading for subsurface conversion of heavy oil to light oil.^{4,6,7} In THAI-CAPRI, the continuous injection of air sustains the combustion front as it moves forward from the toe position to the heel of the horizontal well. The resulting coke lay-down is subsequently burnt as fuel in the process. The heat generated causes oil ahead of the coke zone to flow toward the horizontal well by gravity in a region known as the mobile oil zone (MOZ), where thermal cracking is believed to occur and further upgrading via catalytic cracking takes place as the oil flows across the catalyst layer packed along the horizontal well. The combustion zone can reach temperatures of 450–700 °C which cause heating of the water in the oil layer to generate steam, resulting in steam flooding and/or hot water flooding.^{7–9} The addition of steam to the THAI gases may impact upon the reactions occurring in CAPRI, and thus is important to understand the effect of the reaction gas environment upon the upgrading behavior of CAPRI.

In previous work, Shah et al.¹⁰ found that coke and metals are deposited on the catalyst during reaction and rapidly deactivate the catalyst in the CAPRI section. More recently,

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Hart et al.^{4,11} have reported the use of an activated carbon guard bed on top of the catalyst and hydrogen addition as a remedy for reducing coke formation and sustaining catalyst lifetime. In this study, the effect of steam on the extent of CAPRI upgrading and its contribution to the reduction of coke formation was investigated. Steam is a hydrogen donor via the water–gas shift reaction and this source of hydrogen could promote hydrocracking and hydroconversion reactions. The in situ generated hydrogen could potentially improve the economics of the process compared to surface processing. In addition to reducing the viscosity of the heavy oil, it has been reported that there are chemical reactions between steam and heavy oil which changes the composition of the heavy oil toward the light ends. Hyne and Greidanus¹² describe this chemical interaction between steam and heavy oil as aquathermolysis. The experimental results presented in this paper provide further insight into the extent of aquathermolysis occurring in THAI-CAPRI.

2. EXPERIMENTAL SECTION

This section describes the feedstock, catalyst, reactor rig, and analytical instruments used to measure the changes in physical and chemical properties of the feedstock, produced oil, and spent catalyst.

2.1. Feedstock and Catalyst. The heavy crude oil was supplied by Petrobank Energy and Resources Ltd. from its WHITESANDS THAI Pilot, near Conklin, Alberta, Canada. The crude oil was in fact a blend of partially upgraded oil produced by field THAI trials from eight different wells; the physical and chemical properties of the feedstock are presented in Table 1. The properties of the Co–Mo/ γ -Al₂O₃ catalyst have been reported elsewhere.⁴

Table 1. Properties of the THAI Partially Upgraded Oils

parameter	value
API gravity (deg)	14
viscosity at 20 °C (Pa·s)	1.091
density at 15 °C (g·cm ⁻³)	0.972
sulfur (wt %)	3.52
nickel (ppm)	41
vanadium (ppm)	108
Ni + V (ppm)	149
asphaltene (wt %)	10.3
ASTM D2887 Distillation, °C	
10 vol %	177
30 vol %	271
50 vol %	325
70 vol %	375
90 vol %	440

2.2. Experimental Apparatus. The microreactors used in this study to simulate the conditions of the downhole CAPRI section have been described in detail elsewhere.^{4,10} Briefly, the microreactor is a fixed catalytic bed of 1 cm diameter and 41 cm length. The reactor was loaded in three zones: preheating zone, catalyst bed, and post reaction. The first zone of length 9.3 cm was packed with inert glass beads 3 mm in diameter to ensure homogeneous flow distribution of feed oil and gas, as well as enhance radial contact and prevent axial mixing prior to the catalyst bed. The middle zone is the catalyst bed zone containing 6 g of Co–Mo/ γ -Al₂O₃ catalyst equivalent to 9.11 cm³ volume. The post reaction zone of the reactor was also packed with an inert glass beads to enhance the disengagement of the gas–oil mixture. The reaction was carried out at the previously optimized temperature of 425 °C as determined by Shah et al.¹⁰ and the other conditions are presented in Table 2. Steam was generated by feeding water into traced heated lines having a set temperature of 280 °C and thereafter mixed with the feed oil prior to entering the furnace where the desired

Table 2. Operating Conditions in the Experiments

parameter	value
oil flow rate (mL·min ⁻¹)	1
catalyst inventory (g)	6
pressure (barg)	20
reaction temperature (°C)	425
weight hourly space velocity, WHSV (h ⁻¹)	9.1
gas-to-oil ratio, GOR (mL·mL ⁻¹)	500 or 527.5 Sm ³ ·m ⁻³
steam-to-oil ratio, SOR (mL·mL ⁻¹)	0.02–0.1

experimental temperature of 425 °C is achieved. Therefore, the steam-to-oil ratio (SOR) stated in Table 2 represents milliliters of cold water equivalent (CWE) of water per milliliter of feed oil (CWE/oil) into the CAPRI reactor.

2.3. Analytical Techniques. A Parr DMA 35 density meter was used to measure the density of the feedstock oil, and hence API gravity. An advanced rheometer AR 1000 was used to measure the viscosity of the THAI feed oil and produced oils. ASTM-D2887 was used for determination of the true boiling point (TBP) distribution from a simulated distillation analysis by gas chromatography. An Agilent 7890A gas chromatograph refinery gas analyzer (RGA) was used to determine the volume percentage composition of the produced gases from the CAPRI reactor. A thermogravimetric analyzer (TGA) Model NETZSCH-Geratebau GmbH, TG 209 F1 Iris was used to determine the amount of coke deposited on the spent catalysts. Details of these techniques have been described elsewhere.⁴

The asphaltenes fraction of the heavy oil was obtained by diluting it with straight chain alkanes such as *n*-pentane, *n*-heptane, etc., then collecting the precipitate that forms. The remaining portion thereafter is known as maltene (i.e., mixture of saturates, aromatics, and resins). In this study, the asphaltene fraction was precipitated from the corresponding THAI feed oils and produced upgraded oils using *n*-heptane in accordance to the ASTM D2007-80. Specifically, 1 g of the oil samples was mixed with 40 mL of *n*-heptane. The oil–*n*-heptane mixture was agitated for 4 h using a magnetic stirrer. Thereafter, the mixture was left for 24 h to allow the asphaltenes to precipitate and settle. The precipitated fraction was vacuum filtered using a Whatman 1 filter paper with 11 μ m pore size and 4.25 cm diameter to separate the *n*-heptane soluble portion (maltene) from the asphaltene portion (*n*-heptane insoluble). The filtered asphaltenes were washed with *n*-heptane until a colorless liquid was observed from the filter. The filter paper and precipitate were dried under nitrogen gas flow for 24 h to remove any residual *n*-heptane, then the precipitated asphaltenes weighed.

3. RESULTS AND DISCUSSION

In this section, the results of the experimental runs conducted in triplicate, including API gravity and viscosity measurements, TBP distribution curve of feedstock and liquid products, off-gas composition, and coke content of spent catalyst are presented and discussed.

3.1. Effect of Steam on Mass Balance. The yields of gas, liquid, and coke products after 15 h of catalytic upgrading reactions with and without steam injection are presented in Table 3. It was found that slightly more liquid product was obtained from the process under a steam atmosphere compared with only nitrogen gas.

The liquid product increased by 1.4 wt %, while the coke yield decreased by 0.88 wt % when steam was introduced into the catalytic upgrading process. The increase in liquid yield was expected following the decreased coke and gaseous product yields. This affirms the findings of Gao et al.¹³ that the addition of steam during catalytic upgrading of heavy oil reduces coke formation and increases the yield of light liquid hydrocarbons. During catalytic upgrading (at 425 °C) carbon–carbon bond

Table 3. Product Yields from CAPRI Process without and with Steam at Reaction Temperature of 425 °C, Pressure 20 barg, N₂-to-Oil Ratio 500 mL·mL⁻¹, and Steam-to-Oil Ratio 0.05 mL·mL⁻¹

reaction system	liquid yield (wt %)	coke yield (wt %)	gas yield (wt %)
feed oil + N ₂	93.4	2.11	4.49
feed oil + N ₂ + steam	94.8	1.23	3.97
standard deviation	±0.43	±0.6	±0.14

scissions occur to give lower-boiling hydrocarbons; however, the hydrogen gas generated by the steam inhibits the secondary reactions that lead to coke formation as well as hydrogenates the cracked products, once formed, to increase the yield of liquid product.¹⁴ This occurs because hydrogen can form a radical which becomes involved in chain termination reactions with hydrocarbon radicals. In a steam atmosphere, the amount of produced gases was reduced by 0.52 wt % compared with nitrogen gas, as shown in Table 3. Gao et al.¹³ studied the effect of supercritical water on hydroconversion of heavy residue and pointed out that there is no water-rich phase in the reaction environment since conducted at a temperature of 420 °C.

3.2. Effect of Steam on API Gravity and Viscosity of Produced Oil. In this multiphase system, the following reactions occur: thermolysis, the action of high-temperature steam, and catalytic upgrading. Under these reaction conditions, the large hydrocarbon molecules are pyrolyzed into smaller ones by the steam while the catalytic reactions improve the cracking of the heavy oil and increase its API gravity. In Figure 1a,b, the API gravity and viscosity of the produced oil with and without the injection of steam as a function of time-on-stream are presented. Each data point in Figure 1a,b represents an average of triplicate of experimental run. The maximum observed standard deviations between the experimental runs for API gravity are 0.9 (steam-free), 1.02 (0.02), 0.93 (0.05), and 0.88 (0.1) °API and for viscosity 0.046 (steam-free), 0.065 (0.02), 0.057 (0.05), and 0.038 Pa·s (0.1), respectively. The API gravity of the upgraded oil was higher than the feed oil. There is a noticeable difference in API gravity of the produced oil with and without steam addition. In a steam-free environment, the API gravity increases by a maximum of roughly 6° API during the early part of the experiment and thereafter settles at an average increase of 2.14 ± 1.2 °API for 15 h time-on-stream, from an initial value of 14 °API value for the feed oil. Compared with a maximum increase of 6° using nitrogen, when steam was introduced the API gravity increased to 9° API. Thereafter, the average value settled into the following ranges: 2.5 ± 1.44, 2.93 ± 0.98, and 2.91 ± 1.92 °API for steam-to-oil ratios (SORs) 0.02, 0.05, and 0.1 respectively, for otherwise the same conditions used in the experiment with nitrogen. This indicates a further increment in API gravity of approximately 0.4 to 1 °API upon steam addition above the value obtained in a steam-free atmosphere. The additional increase of 1 °API with steam addition is significant as it may represent a premium of \$2–3 for each barrel of oil produced.⁴ It is therefore clear that 0.05 mL·mL⁻¹ SOR gives the optimum value for improving the API gravity of the produced oil at 425 °C reaction temperature, 20 bar pressure, 500 mL·mL⁻¹ nitrogen-to-oil ratio.

Viscosity reduction is recognized as one of the key objectives of the upgrading processes to promote pipeline transport of the produced oil. From Figure 1b, the viscosity of the produced oil

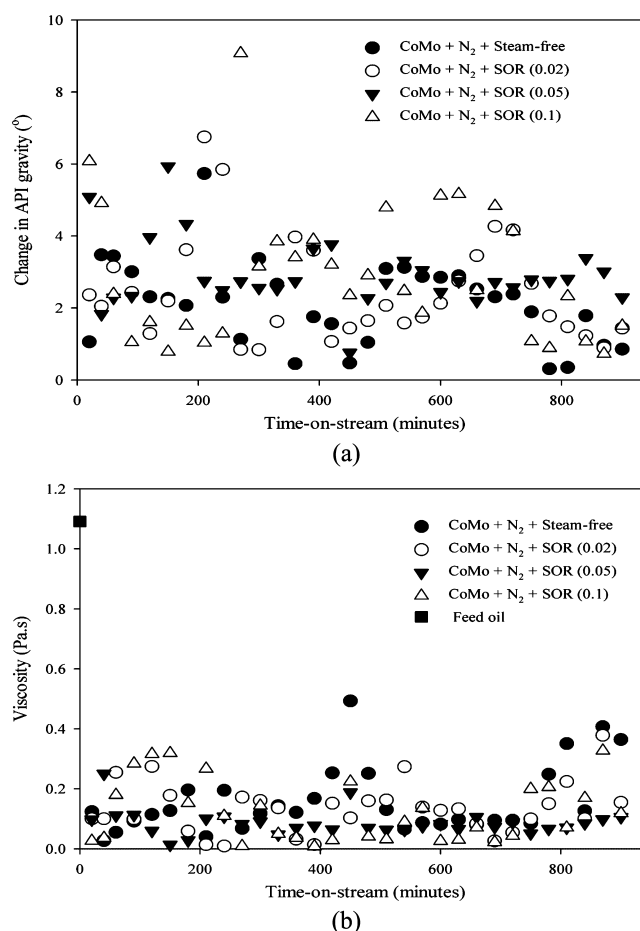


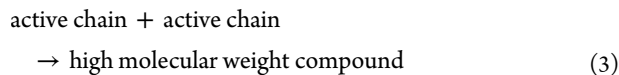
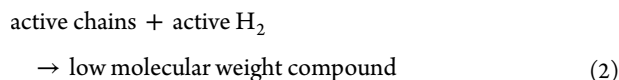
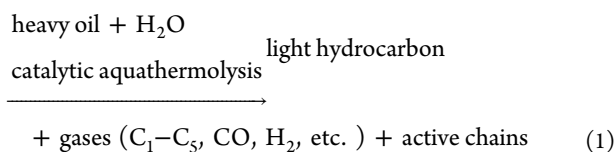
Figure 1. Produced oil using Co–Mo/ γ -Al₂O₃ catalyst. Reaction temperature 425 °C, pressure 20 barg, N₂-to-oil ratio 500 mL·mL⁻¹, steam-to-oil (SOR) ratios 0.02, 0.05, and 0.1 mL·mL⁻¹. (a) Change in API gravity and (b) viscosity as a function of time-on-stream.

in each of the experimental runs is lower than that of the partially upgraded THAI feed oil. It is noteworthy that when there is no steam in the catalytic upgrading process, the average viscosity of the produced oil reduces from 1.091 to 0.158 Pa·s, representing a decrease by 85.5%. However, upon steam-addition, the average viscosity of the produced oil is reduced by 87.8, 92.1, and 89.2%, respectively, as the SOR increases from 0.02 to 0.05 and 0.1 (the percentage error for viscosity measurement in triplicate experimental runs is 1.2%). These data represent a larger decrease in viscosity of 2.3 to 6.6% compared with the value of 85.5% viscosity reduction obtained in a steam-free atmosphere. This shows that the impact of steam-addition on viscosity reduction was comparatively higher than its effect on API gravity increase. The result is in line with the API gravity of the oil produced at the same SOR of 0.05. Li et al.¹⁵ reported 86.1 to 94.7% viscosity reduction after catalytic upgrading in steam atmosphere using Cu²⁺ and Fe³⁺ as catalytic ions for six different heavy oils obtained from China with original viscosities from 22 to 180 Pa·s at 50 °C. A similar trend of observation was also reported by Fan et al.¹⁶ and Maity et al.¹⁷ It also suggests that steam addition to the process is able to affect further upgrading than catalytic carbon rejection which is thought to occur with only nitrogen.

In addition to the fact that steam can reduce the viscosity of heavy oil, there are chemical reactions between steam and heavy oil in the presence of catalyst.¹⁶ Chuan et al.¹⁸ and Wang

et al.¹⁹ found that during catalytic upgrading of heavy oil in a steam atmosphere, the steam not only acts as a solvent, reactant, and hydrogen donor but also aids the production of acid sites by interacting with catalytic metals and contributes to many reactions such as catalytic cracking, hydrogenation, ring-opening, and desulfurization involving the splitting of C—S, C—N, C—O, C—C, C=S, and C=O bonds. These reactions affect viscosity reduction, increase API gravity, remove heteroatoms, and improve the produced oil quality. Additionally, in situ hydrogen generation via the water–gas shift reaction will help reduce the chances of recombination of free radicals or active chains formed by the cleavage of C—C, C—S, C—N, and C—O bonds to form large molecules by terminating the active chains.¹⁷

Fan et al.²⁰ attributed these compositional changes and viscosity reduction of the produced oil to the synergistic effects of catalyst and steam. It is clear that this synergistic effect of the catalyst and steam improved the cracking behavior and the yield of light fractions of the oil as reflected in the API gravity and viscosity reduction. This can be illustrated by the reactions in eqs 1–3 below:



Li et al.¹⁵ pointed out that the acid sites of the catalyst cracks the C-heteroatom bonds of the macromolecules of the heavy oil, in which the C—S, C—N, and C—O bonds are weakened and the injected steam interaction with these bonds facilitates cleavage. During crude oil production, oil flow is inversely proportional to its viscosity through the porous reservoir matrix, as very light oil has enough mobility that aids production by natural reservoir pressure or water flooding. From the results above, it is therefore interesting to note that the 87 to 92% viscosity reduction in the steam assisted catalytic upgrading process is capable of producing oil with the required fluidity to ensure an improved rate of recovery, and consequently pipeline transport with little or no diluent addition.

3.3. Effect of Steam Addition on Distillable Yields. Simulated distillation provides the true boiling point (TBP) distribution of hydrocarbon fractions in the samples (the horizontal axis in Figure 2 shows the boiling temperature and the vertical axis displays cumulative amount distilled). The experimental errors in the distillable yields in this study were estimated as standard deviation within $\pm 4.6\%$ for triplicate run. Figure 2 shows the TBP distribution curves for the feed and produced oils with Co—Mo/alumina catalyst when the reaction was carried out under a nitrogen atmosphere only and in combination with steam at the different SOR. The feed oil TBP curve is presented for the purpose of comparison. The effect of steam-addition on the conversion of heavy fractions and the production of lighter fractions is illustrated by the shift in TBP curves of the produced oil to the left, indicating that the

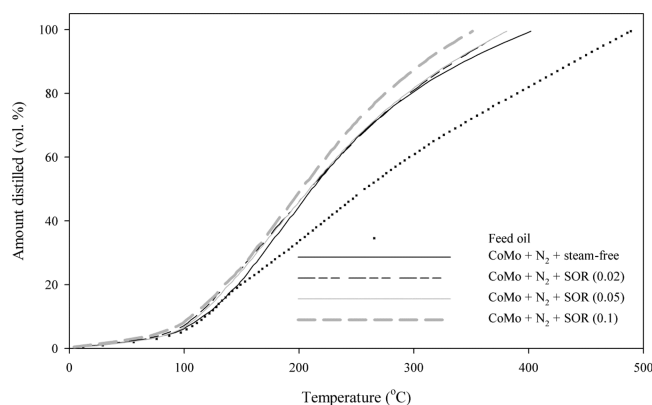
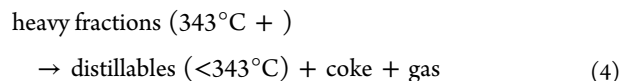


Figure 2. TBP distribution curves for feed and produced oils using Co—Mo/ γ -Al₂O₃. Reaction temperature 425 °C, pressure 20 barg, N₂-to-oil ratio 500 mL·mL⁻¹, and SORs 0.02, 0.05, and 0.1 mL·mL⁻¹.

produced oil contains lower boiling components than the feed oil. Thus, the cumulative amount distilled at a boiling temperature of 343 °C increases from 70.5% in the feed oil to 89.8% in nitrogen atmosphere alone. However, when steam was added this value rose to 97.2, 92, and 91.6% for SORs 0.1, 0.05, and 0.02, respectively.

Compared to the feed oil, catalytic upgrading improved the distillate yield by up to 20% which is thought to occur mainly through carbon rejection with limited indirect hydrogenation in a steam-free atmosphere. It was concluded from the results that a higher steam injection rate improves the yield of light hydrocarbon fractions. The additional 1 to 7% increase in distillates yield as a result of steam injection can be attributed to the hydrogenation of cracked fragments by the hydrogen generated from water gas shift reaction of steam and carbon monoxide within the upgrading media. This therefore indicates an increase in the percentage of middle fractions (i.e., 200–343 °C) in the produced oil due to the hydrogen donor ability of steam. A similar increase in the amount of middle distillates was found when pure hydrogen was added to the reaction media during catalytic upgrading process.⁴

From the TBP curves, it can be inferred that some of the heavy molecular weight hydrocarbons in the partially upgraded THAI feedstock have been converted to hydrocarbons of the middle distillate fractions (i.e., boiling point 200–343 °C) whereas the middle fractions are converted to light hydrocarbons (i.e., initial boiling point (IBP) to 200 °C), gases (C₁–C₅), and coke. In this regard, the conversion of high-boiling-point (high molecular weight) fractions to lighter fractions (boiling less than 343 °C) occurs by thermal and/or catalytic cracking, expressed by eq 4:



The distillables consist of light oil and medium oil fractions in the produced oil. Therefore, the conversion is determined as follows:

$$\text{conversion} = \frac{(343^\circ\text{C} +) \text{ HC in feed} - (343^\circ\text{C} +) \text{ HC in product}}{(343^\circ\text{C} +) \text{ HC in feed}} \quad (5)$$

In Table 4, the conversion of 343 °C+ HCs as a function of SOR is presented. It is clear that the conversion increased as the SOR increased from 0.02 to 0.1. It can be seen in Figure 2

Table 4. Conversion of 343 °C+ HCs to Lower Boiling Fractions at Reaction Temperature of 425 °C, Pressure 20 barg, N₂-to-Oil Ratio 500 mL·mL⁻¹, and Varying SOR Using Co–Mo/Alumina Catalyst

SOR (mL·mL ⁻¹)	conversion (%)
no steam	65.4
0.02	71.5
0.05	72.9
0.1	90.5

that there is a greater impact on conversion above 343 °C. For instance, the production of the distillate fractions in the range of temperature (200–380 °C) is higher compared to distillates in the lower temperature range (100–200 °C). The further shift of the TBP curve for SOR of 0.1 to the left (between temperatures 200–380 °C), relative to that without steam addition, means that there is a higher proportion of lighter components when SOR = 0.1 and is accompanied by a reduction in the viscosity from 1.091 to 0.121 Pa·s. The simulated distillation (SIMDIS) results provide an explanation of why most of the macromolecules in the feed oil are converted to middle distillates, rather than lighter fractions. Similar trends were also reported for HDS catalysts on hydrocracking of atmospheric residue.^{21,22}

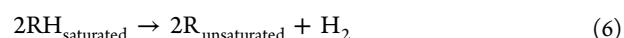
Wang et al.¹⁹ reported a similar improvement in the amount of distillate yield from oil produced after catalytic upgrading of heavy oil in a steam environment using tungsten oxide on zirconia (W/Zr) catalyst. This can be attributed to the synergistic effect of steam-distillation and consequent transfer of heat energy from the steam to hydrocarbons that breaks the large molecules into smaller ones in addition to catalytic cracking reactions and hydrogenation.

3.4. Effect of Steam on Gas Composition. The results of the RGA analysis for gas composition are given in Table 5. The

Table 5. Produced Gas Composition during Catalytic Upgrading Reaction in Nitrogen Atmosphere Only and in Combination with Steam Using Co–Mo/γ-Al₂O₃ Catalyst at Reaction Temperature of 425 °C, Pressure 20 barg, N₂-to-Oil Ratio 500 mL·mL⁻¹, and different SORs

gas	no steam (vol %)	SOR (0.1) (vol %)	SOR (0.05) (vol %)	SOR (0.02) (vol %)
methane	2.33	1.15	1.27	1.46
hydrogen	2.4	1.37	1.1	1.41
Ethane	0.82	0.06	0.033	0.03
carbon dioxide	0.03	0.07	0.064	0.054
ethene	0.03	0.07	0.08	0.073
propane	0.23	0.21	0.15	0.113
Propene	0.14	0.10	0.07	0.068
<i>i</i> -butane	0.12	0.14	0.03	0.062
<i>n</i> -butane	0.06	0.14	0.03	0.073
1-butene	0.051	0.035	0.034	0.044
<i>cis</i> -2-butene	0.00	0.037	0.029	0.038
<i>trans</i> -2-butene	0.02	0.033	0.00	0.023
<i>n</i> -Pentane	0.19	0.11	0.064	0.11
<i>i</i> -pentane	0.17	0.07	0.034	0.064
carbon monoxide	0.02	0.016	0.018	0.019
hydrogen sulfide	0.00042	0.00052	0.00044	0.00043

off-gases are products of the upgrading reactions resulting from the splitting of large molecules into smaller ones. The gas composition provides further insight into the reaction mechanism. The presence of hydrogen in the off-gas indicates the potential of the process to generate hydrogen in the reservoir. Notably, 2.4 vol % of hydrogen was detected at the reactor outlet in a steam-free atmosphere versus 1.1–1.4 vol % in a steam atmosphere depending on the SOR. This decrease in hydrogen volume is deduced to be because some of the generated hydrogen is consumed in hydrogenation, hydrodesulfurization (HDS), hydrodemetallization (HDM) reactions, and the inhibition of hydrogen abstraction from macrohydrocarbon molecules, leading to coke formation, even though additional hydrogen may be generated in the presence of steam. The evolved hydrogen originates from two reaction routes: first through hydrogen subtraction from the excited saturated hydrocarbon to form an unsaturated hydrocarbon molecule as illustrated by eq 6:



where, R is a hydrocarbon molecule.

C–H bond cleavage produces hydrocarbon radicals and active hydrogen. The active hydrogen on collision with another molecule abstracts hydrogen to form a hydrogen molecule, as illustrated by eqs 7 and 8.²³ In this way, the macromolecule structure continues to grow further while the free radical sites at the formed coke surface are revived by continuous hydrogen abstraction.^{24,25} The free radicals formed, unsaturated molecules and aromatics, are common coke precursors. They promote coke formation by terminating reactions with coke macroradicals. Alternatively, the active hydrogen can react with other hydrocarbon radicals to form a stable molecule by hydrogenation. Reactions 6–8 could have been inhibited by injection of steam as hydrogen donor.

Consequently, the total olefin content of the produced gas is as follows: 0.241 vol % (steam free), 0.31 vol % (SOR, 0.1), 0.242 vol % (SOR, 0.05), and 0.246 vol % (SOR, 0.02). Under the same conditions, the paraffinic contents are, respectively, 3.92 vol % (steam free), 1.804 vol % (SOR, 0.1), 1.661 vol % (SOR, 0.05), and 1.912 vol % (SOR, 0.02). It is clear, therefore, that the presence of steam limits olefin saturation.¹³ Furthermore, when steam was introduced to the catalytic upgrading process, less gases such as light hydrocarbons (i.e., C₁–C₅), carbon monoxide, and hydrogen were produced, because, in the presence of steam, the catalyst accelerates aquathermolysis of the oil, in addition to hydrogenation. However, an increase in carbon dioxide production was observed, from 0.03 vol % (steam free) to 0.054, 0.064, and 0.07 vol %, as the SOR was increased from 0.02 to 0.05 and 0.1. This is because the water–gas shift reaction occurs within the upgrading media. The lower gas production in the presence of steam is consistent with result of the mass balance presented in Table 3 and with the result reported by Fan et al.²⁰

The two reaction routes for sulfur removal are the following: direct removal of the sulfur atom from the straight chain molecule and hydrogenation of aromatic rings, followed by removal of the sulfur atom.²² Upon the injection of steam, the amount of hydrogen sulfide in the produced gas increased from 0.000 42% (steam free) to 0.000 52% for SOR of 0.1, indicating that additional C–S bonds in the sulfur-containing compounds

of the feed oil have been ruptured and converted to H_2S . The removal of the sulfur as hydrogen sulfide demonstrates that a HDS reaction occurred during the catalytic upgrading process and the injection of steam increased the extent of conversion. The amount of methane and hydrogen in the off-gas decreased with the increasing amount of added steam. The results were consistent with those reported in the literature.^{17,26} The decrease in the amount of methane with increase in steam addition can be attributed to the following reactions (see eq 9) postulated by Hongfu et al.:²⁶



The observed decrease in the amount of hydrogen was attributed to in situ HDS, hydrogenation of the free radicals, and olefins produced during the process.²⁶

3.5. Water–Gas Shift Reaction. In Figure 3, the produced carbon dioxide and carbon monoxide gases are presented as a

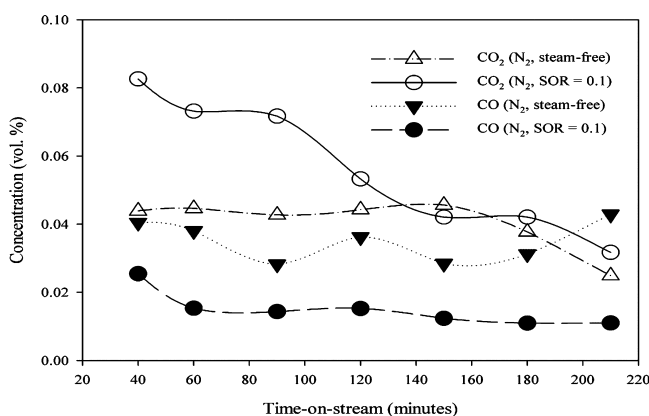


Figure 3. CO_2 and CO production during catalytic upgrading in the presence and absence of steam at temperature of 425°C ; pressure, 20 barg; SOR, $0.1\text{ mL}\cdot\text{mL}^{-1}$; N_2 -to-oil ratio, $500\text{ mL}\cdot\text{mL}^{-1}$.

function of time-on-stream, for nitrogen only and nitrogen with steam addition. It is clear that steam addition increased the amount of carbon dioxide gas produced while carbon monoxide decreased. The generation of carbon dioxide can be attributed largely to the water–gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} (\text{g}) = \text{CO}_2 + \text{H}_2$, $\Delta H = -41.1\text{ kJ}\cdot\text{mol}^{-1}$) that occurs in the presence of steam, catalyst, and CO generated from aquathermolysis of heavy oil.²⁰ It is also noteworthy the increased amount of carbon dioxide and the decreased amount of carbon monoxide in the outlet gas in the presence of steam provides evidence that the WGS reaction occurred to a greater extent with the addition of steam. It can also be seen from Figure 3 that the carbon dioxide produced via WGS reaction decreased with time-on-stream, because of loss of catalytic activity resulting from coke deposition.

The redox mechanism assumes that the catalyst surface is oxidized by H_2O , producing H_2 as byproduct, followed by reduction on the active sites on the surface to convert CO at high reaction temperature, as shown in the eq 10 and 11:²⁷



Therefore, during the upgrading reaction, water acts as a hydrogen donor, providing the required hydrogen for hydrogenation and HDS.

Carbon dioxide can help to decrease the oil viscosity via miscible and/or immiscible displacement and improve recovery of heavy oils. At the same time, the $\text{C}_2\text{--C}_5$ light hydrocarbons act as solvent that can also reduce the viscosity of heavy oil, enhance oil displacement via miscible gas displacement in the reservoir matrix, and improve the oil flow properties during THAI-CAPRI recovery and upgrading process. Carbon dioxide generated in situ via water–gas shift (WGS) reaction could be potentially sequestered in the reservoir so that emissions to the atmosphere are reduced.²⁸ Li et al.¹⁵ and Hongfu et al.²⁶ pointed out that the increased amount of carbon dioxide that is generated by steam injection may partly be attributed to the decarboxylation of carboxylic derivatives in the heavy oil in addition to the WGSR.

3.6. Asphaltenes, Sulfur, and Metals Content. It is well-known that heavy oil and bitumen are rich in asphaltenes, containing roughly 10–30 wt %, which strongly affects the viscosity as well as contaminants such as heavy metals, sulfur, and nitrogen.²⁹ In Table 6, the asphaltenes, metals and sulfur

Table 6. Asphaltenes, Sulfur, And Metals Content before and after CAPRI Reaction with and without Steam Addition at Reaction Temperature of 425°C , Pressure 20 barg, N_2 -to-Oil Ratio $500\text{ mL}\cdot\text{mL}^{-1}$, and different SORs^a

impurities	feedstock	no steam	SOR (0.02)	SOR (0.05)	SOR (0.1)
asphaltene (wt %)	10.3	5.1	5.1	4.9	2.4
aluminum (ppm)	2	2	<1	1	<1
boron (ppm)	3	2	1	1	<1
iron (ppm)	5	<1	1	<1	<1
nickel (ppm)	41	34	30	23	12
vanadium (ppm)	108	90	78	62	32
Ni + V (ppm)	149	124	108	85	44
sulfur (wt %)	3.52	3.4	3.08	2.95	2.62
silicon (ppm)	1	<1	<1	<1	<1

^aSulfur and metals content was performed by Intertek Laboratories Sunbury Technology Centre, UK, using ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry).

content of the feed and selected produced oil samples, without steam and with different SORs are presented. Interestingly, the asphaltenes content of the upgraded oils decreased from 5.1 wt % in a steam-free environment to 4.9 and 2.4 wt % as the SOR increased from 0.05 to 0.1. Hyne and Greidanus¹² and Fan et al.³⁰ investigated aquathermolysis and catalytic aquathermal cracking of heavy oils and found that after reaction the saturates and aromatics increased, while the resins and asphaltenes decreased. Thus, the decreased amount of asphaltenes content correlated with viscosity reduction and improved distillable yields. This trend is consistent with the literature.^{17,26}

The saturates fraction is the lightest and consists mainly of paraffinic and naphthenic molecules. Therefore, the compositional shift of the upgraded oil toward the low boiling temperature fractions after catalytic upgrading reactions, as shown in the TBP curves in Figure 2, is an indication of increased saturate content. As the active oxygen and hydrogen generated from steam over the catalyst reacts with the heavy oil fractions to produce lighter fractions and carbon dioxide, the hydrogen terminates free radical addition reactions and increases the saturates and aromatic content of the produced oil.^{31,32}

The results are analyzed as percentage of impurities removed through desulfurization, demetallization, and deasphaltenization using eq 12:

$$\% \text{removal} = \frac{(C_{\text{feed oil}} - C_{\text{oil produced}})}{C_{\text{feed oil}}} \times 100 \quad (12)$$

where $C_{\text{feed oil}}$ and $C_{\text{oil produced}}$ are the amount of sulfur, metals and asphaltenes in the feed oil and produced oil, respectively.

From Table 6, the sulfur content of the produced oils decreased from 3.52 wt % for the feedstock to 3.4 wt % without steam addition, and 3.08, 2.95, and 2.62 wt %, as SOR increased from 0.02 to 0.05 and 0.1 mL·mL⁻¹, respectively. This indicates sulfur removal of 3.4% (no steam), 12.2% (0.02 SOR), 16.2% (0.05 SOR), and 25.6% (0.1 SOR), with the trend increasing as the SOR increased. The significant reduction of sulfur content upon steam addition provides evidence that a greater degree of C–S bond cleavage occurred in a steam atmosphere. This is because steam addition promoted HDS reactions which were evident from the high concentration of hydrogen sulfide in the off-gas analysis (Table 5). Nevertheless, it has been widely reported in the literature that the mechanism for viscosity reduction during catalytic upgrading of heavy oil in the presence of steam is based on the theory of C–S bond breaking.^{15,20,33,34} There, it was pointed out that the C–S bond is one of the weakest bonds among heavy oil molecules; therefore, the additional increase in the viscosity reduction of the produced oil relative to the feed oil and that obtained in a steam-free atmosphere can be attributed to increased HDS reactions during the catalytic upgrading process in steam atmosphere (Table 6). This is because steam possesses hydrogen donor ability through water–gas shift reaction, where water participated as reactant and solvent.¹⁵ Second, the increased SOR provides more active hydrogen through water–gas shift reaction. This helps to explain the additional 2.3 to 6.6% viscosity reduction above the value of 85.5% obtained under a steam-free atmosphere.

Concurrent with the trends in sulfur removal, the nickel and vanadium (Ni + V) content of the produced oils was reduced from 149 ppm in the feedstock to 124 ppm for steam-free atmosphere and with injection of steam to 108, 85, and 44 ppm as SOR increased from 0.02 to 0.05 and 0.1, respectively. The demetallization reactions for removal of (Ni + V) increased from 16.8% in steam-free environment to 43 and 70.5% as the SOR increased from 0.05 to 0.1, respectively. This indicates 26–54% further reduction of (Ni + V) content upon steam addition. The reduction in sulfur and metals content of the oil produced is consistent with the conversion of asphaltene molecules. It is possible that this significant reduction in the metal content of the produced oil contributed to the 1° increase of API gravity with steam addition above that without steam, because the presence of metals influences the heavy oil density. Additionally, the donated hydrogen via WGSR therefore promoted hydrodemetallization (HDM) reactions, which is not experienced to the same extent in steam-free environment. Moreover, the concentrations of other impurities such as aluminum, boron, and iron were also reduced significantly in a similar trend. These metals are transformed to metal sulfides and deposited onto the catalyst with their accumulation causing catalyst deactivation.³⁵

3.7. Catalyst Coke Content. In previously reported work, it was found that coke formation in the catalytic upgrading process can be suppressed by adding hydrogen.^{4,36} In this

study, steam addition was investigated as a potential source of hydrogen via WGS reaction. TG and differential thermogravimetric (DTG) analysis of the spent Co–Mo catalyst recovered from the CAPRI reactor after upgrading reactions with and without steam injection is presented in Figure 4. The spent

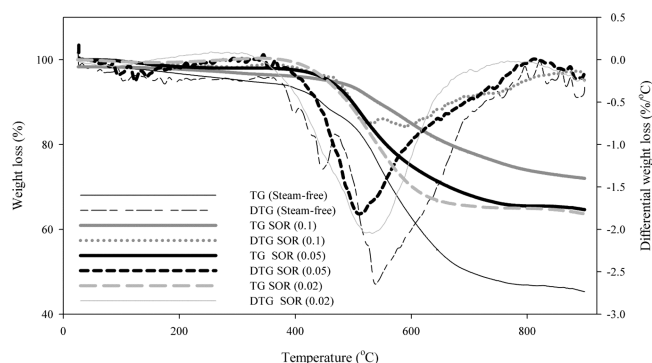


Figure 4. TG and DTG of fresh and spent Co–Mo catalyst recovered from CAPRI reactor after reaction with and without steam addition at reaction temperature of 425 °C, pressure 20 barg, and N₂-to-oil ratio 500 mL·mL⁻¹.

catalyst contains unconverted oil, cracked oil products and intermediates, and coke. The latter starts to burnoff at about 530 °C during TGA analysis.^{4,36} In Table 7, the coke content of

Table 7. Spent Co–Mo Catalyst Coke Content after CAPRI Upgrading with and without Steam Addition at Reaction Temperature of 425 °C, Pressure 20 barg, and N₂-to-Oil Ratio 500 mL·mL⁻¹

SOR (mL·mL ⁻¹)	spent catalyst coke content (wt %)
no steam	27.53 ± 1.43
0.02	21.81 ± 0.94
0.05	18.07 ± 0.86
0.1	16.23 ± 1.09

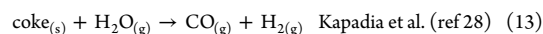
the recovered spent catalyst is presented. The recovered catalyst from the CAPRI reactor after an upgrading experiment was carried out in a steam atmosphere showed lower coke content compared to the experiment in nitrogen atmosphere only.

The feed oil cracked over the Co–Mo/alumina catalyst at 425 °C yields light hydrocarbon fractions, gas, and coke. In previous work by Hart et al.,⁴ it was found that in a steam-free atmosphere, a large amount of coke was formed on the catalyst, resulting in reactor plugging and rapid catalyst deactivation. However, in a steam atmosphere, the coke content of the catalyst decreased from 27.53 wt % (steam free) to 21.81, 18.07, and 16.23 wt % as the SOR increased from 0.02 to 0.05 and 0.1, respectively. In this respect, the coke content was reduced by 5.72–11.3 wt % as SOR increased in the range of 0.02–0.1. Consequently, the DTG curves indicate that the coke formed in the presence of steam started to burnoff at a lower temperature of approximately 521 °C compared with the coke formed in a steam-free atmosphere which starts to burnoff about 539 °C. These results also provide evidence that steam was involved in the catalytic upgrading reactions, as hydrogen donor solvent. The 18 °C difference in burnoff temperature is thought to arise from structural differences in the coke molecules. The impact of steam addition on reduction of

catalyst coke is significantly higher compared to that of API gravity increase and viscosity reduction.

Although SOR of $0.05 \text{ mL} \cdot \text{mL}^{-1}$ gave the optimum degree of upgrading in terms of API gravity and viscosity of produced oil, the largest decrease of coke content of 11.3 wt % relative to the experiment without steam occurred at the higher SOR of $0.1 \text{ mL} \cdot \text{mL}^{-1}$. This coke reduction was 1.84 wt % higher than the value of 9.46 wt % reduction that occurred at a SOR of $0.05 \text{ mL} \cdot \text{mL}^{-1}$. Therefore, a trade-off between coke reduction and degree of upgrading with steam-to-oil ratio is required. Furthermore, Maity et al.¹⁷ pointed out that the addition of a small amount of water depressed coke formation, with the coke content of catalyst decreasing with additional steam and leveled off after 10 wt % of steam. This is thought to be because the high SOR increased the generation of active in situ hydrogen for hydrogenation reaction. Fumoto et al.³⁷ pointed out that at lower steam flow rate, there is inadequate generation of these active species, causing coke build-up on the catalyst. Because the reaction medium has insufficient hydrogen-transfer capability at low SOR, free radical propagation could not be adequately moderated. This is supported by the decrease in the methane and hydrogen concentration in the off-gas as the SOR decreased from 0.1 to 0.02.¹⁴

The decreased coke deposition due to steam addition can be attributed to the reaction between steam and coke, generating carbon monoxide and hydrogen.²⁸ This produced hydrogen can further react with coke as a precursor to form methane; details of the reactions are presented in eqs 13 and 14. In addition, Fumoto et al.³⁷ reported that active oxygen and hydrogen are produced from steam over the catalyst (see eqs 15 and 16). The reaction between the coke and active oxygen can also help to suppress coke build-up.³¹ Some of the produced hydrogen is utilized to stabilize unsaturated and unstable hydrocarbons products such as olefins and coke precursors.



In the work of Fumoto and co-workers³⁷ it was shown that the reaction of oxygen generated from steam with the heavy oil over the catalyst produced an appreciable amount of light oil and carbon dioxide with a lower amount of coke. Also, Sato et al.³² pointed out that the presence of a hydrogen donor (through WGS reaction) in the oil-rich phase is effective for suppression of coke formation during the catalytic upgrading process. Coke formation mostly occurs in the oil-rich phase by polymerization of high molecular weight poly aromatic cores.

4. CONCLUSIONS

The effect of steam addition in the catalytic upgrading of heavy oil downhole was investigated at the following reaction conditions: temperature 425°C , pressure 20 bar, gas-to-oil ratio of $500 \text{ mL} \cdot \text{mL}^{-1}$, and steam-to-oil ratio in the range of 0.02 to 0.1. It was found that viscosity reduction of the produced oil was 2–7% higher in the presence of steam compared to that obtained in a steam-free atmosphere. The API gravity and distillate yields also improved with higher SOR. In the reservoir, water can be activated through the water–gas shift reaction to provide in situ hydrogen, assisted by mineral ions in the rock formation in addition to the catalyst

surrounding the horizontal well in CAPRI. The hydrogen produced contributes toward hydrogenation of cracked products, HDS, and HDM reactions. It was also found that the coke content on the spent catalyst coke after catalytic upgrading decreased significantly as the SOR increased from 0.02 to 0.1. Co–Mo/alumina catalyst promoted both WGS reaction to provide in situ hydrogen for HDS and upgrading reactions while suppressing coke production. It was also found the sulfur and metals (Ni + V) content removal increased by 8.1–22.2% and 26–54%, respectively, when steam was introduced, compared to 3.4% and 16.8% in a steam-free atmosphere.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

HDS = hydrodesulfurization
HDM = hydrodemetallization
TGA = thermogravimetric analysis
DTG = differential thermogravimetric
RGA = refinery gas analyzer
WGSR = water–gas shift reaction
CAPRI = catalytic upgrading process in situ
THAI = toe-to-heel air injection

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